Studies on removal of malachite green dye from aqueous solution using plant based biosorbents

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Studies on removal of malachite green dye from aqueous solution using plant based biosorbents

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Under the supervision of

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We, the below signed, after checking the dissertation mentioned above and the official record book of the student, and hereby state our approval of the dissertation submitted in the partial fulfilment of the requirements of the degree of Masters in Biotechnology and Medical Engineering at National Institute of Technology, Rourkela. We are satisfied with the volume, correctness, quality, and originality of the work.

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This is to confirm that the Thesis entitled *"Studies on removal of malachite green dye from aqueous solution using plant based biosorbents*" by Sujata Lata submitted to the National Institute of Technology, Rourkela for the honour of Master of Technology in Biotechnology during the session 2015-2017 is a record of bonafide research work done by her in the Department of Biotechnology and Medical Engineering under my supervision and guidance. To the best of my knowledge, the matter contained in this thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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Declaration of Originality

I, Sujata Lata, Roll Number 215BM2008 hereby declare that this dissertation entitled “Study of biosorption of malachite green dye from aqueous solution using plant based biosorbent”: A disaggregation study presents my original work carried out as an M.Tech student of NIT Rourkela and, to the best of my knowledge, contains no materials previously published or written by any other person, nor any material presented by me, for the award of any degree or diploma in NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. I have also submitted my original records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the senate of NIT Rourkela may withdraw the degree awarded to me on the basis of this present dissertation.

May’24, 2017

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Abstract

The removal of malachite green dye from wastewater is carried out using papaya wood, banana peel, and bael shell as biosorbents. Batch scale biosorption studies were carried out to evaluate the effect of various parameters such as time of contact, temperature, initial pH, biosorbate dosage and the suitable criteria for these factors were estimated. It was found that the effective time of contact for better dye removal performance was around 140 min at the dye concentration of 10 mg/l for all the three biosorbents. The removal efficiency of biosorbents was found maximum at pH 10 for papaya wood, at pH 7 for banana peel and at pH 8 for bael shell. Moreover, the optimum doses of these biosorbent materials were estimated at 0.06, 0.1 and 0.12 g/100 ml for papaya wood, banana peel and bael shell respectively. Maximum removal of dye was achieved at temperature 50°C for all the three biosorbents. Isotherm study of biosorption was done as well as the suitable fitting isothermal models were also demonstrated. Isotherm of Langmuir and Freundlich concepts were utilized to fit the equilibrated data and the outcomes showed that the Langmuir concept appeared better than Freundlich's one. The results showed that papaya wood, banana peel and bael shell are proficient to use as an alternative for treating effluents which have malachite green in the water sample.

Keywords: Biosorption; Isotherm; Biosorbents; Temperature; Initial dye concentration; Malachite green; Dye

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Chapter 1

Introduction

1.1 Dye

A dye acts as staining matter which has an intrinsic property to get a colour to the surface of substance on which it is being used [1]. In many fields, the state of dye occupies the form of liquid solution mixtures. Dyes are used in staining different substrates like paper, textiles, plastic, leather etc. in an aqueous form [2]. The dye's characteristic is to get partially or completely solubilised in which it is being applied. The application of dye is as similar as other chemical according to the rule. As an example, some certain type of dyes may be toxic, mutagenic or carcinogenic and may cause as a harmful to health [3]. For showing the better efficiency of .dye on the fibre, some other substances called mordant is applied as the catalyst. Both pigments and dyes are appeared to be stained because they respond specific wavelength of light rather than others. There are many reasons due to which substance get coloured; the common justification is as that it absorbs in the range of 400 to 700 nm [4, 5]. Even because they hold colour-bearing site of groups so called chromophores, it has proficiency in their propensity to draw up radiation. Chromophores show its actions by making energy changes by the transition of the electron cloud's delocalisation of the dye [6]. Also, the dyes' structure shows single and double bonds consecutively and the final fact is that dyes' molecule possesses resonance characteristics which stabilise organic matters [7]. The chemicals fail to retain its colour when any of these conditions satisfy them. Dyes are also the content of another matter is said as auxochromes which are in layman language known as colour helpers. The carboxylic acid group, sulfonic acid group, amino-group, and hydroxyl groups are generally some of the auxochromes. Auxochromes are not well defined for causing the stain in the colourant but are applied in changing the solubility of dye [8]. The dyes are classified as two categories i.e., naturally occurring matter and synthetic or artificial one. The colourants, which are got from plants or any natural resources, are known natural matters. A large amount of natural staining matter is got from plant sources for example leaves, roots, bark and tree wood [9].

The presence of colour in dye and its conducive compounds have been showing always unusual property when get exposed with an aqueous surface for the use in either domestically massive purpose or industrially mass requirements.

Different types of colouring substances like lignin, dyes, inorganic pigments, tanning etc. are all important colour [10]. Dye wastes are major among complicated effluent from industries with abundant sort of colouring matters. There are beyond eight thousand different types of staining dye pigment in a market which is possessing different chemical characteristics [11].

1.2 Harmful Effects of Dyes

Due to extensive application and production on large-scale, dyes cause remarkable pollution in the environment and are very serious fatal diseases. Even though, the incoming impact of protection of environment on development of industries promotes the reduced consumption of freshwater, the development of eco-friendly technologies, government law related to environment issue and is a serious headache to scientists of environmental study background [12].

All the waste dyes, which are extracted from different types of industries, may have hazard effects on microbes, aquatic organisms and can be toxic and even tend fatal to mammals. These colours can cause of inducing for mutations and cancer, an irritating problem in skin, allergic eczema. The few chemical compounds are applied to produce dye which may be carcinogenic, highly toxic, and hormonal disruptive factor [13]. The excessive applying of dye pigments results from ecosystem imbalance in nature. This is not exclusively resisted penetration of sun rays into water-body and reduces photosynthesis but also comes out as leading atmospheric obstructs.

The pigment of malachite is harmful stains which do not only possess largely pernicious. Factors impacting on the mammalian cell lines and tissues but also plays the major role in inducing tumour in liver tissue [14]. The dye that is exposed in water sources with no filtration processes obstructs the life-cycle process of organisms in aquatic environment and plants by resisting the penetration of sunlight. In order to sustain aquatic life, these make scarcity of dissolved oxygen amount due to consecutively boost in the BOD [15, 16]. Since a few of dye pigments are awfully cyanogens, they cause hazard of their abilities in chemical action process. At low magnitudes, the dye has a huge impact on the lifespan of marine animals, plants and meanwhile, it also reaches the food chain [17]. According to its composition, colours are the extremely stable chemical component, manufactured to struggle against the light degradation, aspects of a biological issue, chemical compound and other corners [18].

1.3 Removal Methods

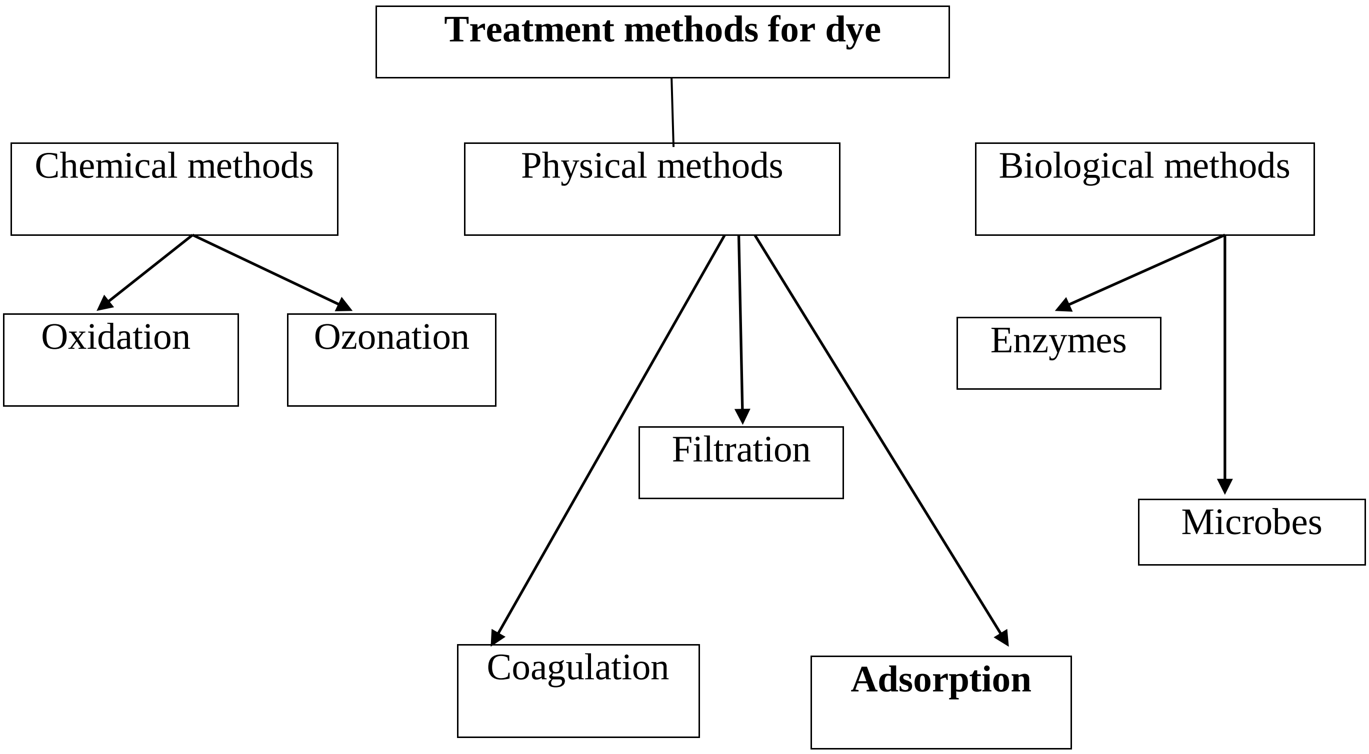

Figure 1: Treatment methods of dye from an aqueous solution.

The removal of dye is the most tedious jobs for the dye producing, fisheries purpose, tannery industries and bleaching of Kraft and paper and pulp matter among others. Membrane separation, chemical process in oxidation etc. are the different methods applied to filtrate colours from waste effluent. Other procedures are an electrochemical method, anaerobic or aerobic processes, agglomeration process etc. Due to so much expensive and non-proficient, many of these methods are not applied on large magnitude scale. Coagulations action, chemically as well as electrochemically oxidations are less-efficient on higher scale plants [19, 20]. Biosorption process is an advantage over the reaction process and is deployed as broad spectrum due to its economic cost and higher efficiency. A carbon of activated form is the most usually utilised as well biosorbing matter [21, 22].

Alumina, silica, hydroxides of metal etc. are other elements. Economical cost, performance efficiency and environment are major aspects while selecting an adsorbent, therefore scientist always chooses best and cheap adsorbents such as char which is a waste matter [23].

An activated carbon is selected as biosorbent in many systems of industries to remove dyes in waste effluent attributed to its remarkable biosorption efficiency [24, 25]. Numerous literature outcomes elucidated that much lower fare materials are been successfully applied for the colours from liquid solution mixtures exclusively [26]. However, a very few of these can able to biosorb expertly to filtrate dye pigment from the effluent stream-line. Hence, by this project, the efficiency of another naive waste material which is obtained abundantly in India is discovered.

1.4 Objective of the present work

The purpose of the project work is

1. To prepare and characterise the biosorbents from papaya wood, banana peel and bael shell.
2. To study the various influencing factors of biosorption including pH, biosorbent dosage, initial dye concentration and temperature etc.
3. To evaluate the various isotherm model for understanding the biosorption kinetics.

Chapter 2

Literature Review

2.1. Adsorption

Biosorption is activity in which molecular particles, atoms and ions of the liquid or gas gets adhesively bound to the surface of any matter [27]. Biosorbate is in liquid form which gets surrounded on the solid adsorbent's surface. In adsorption, there is contact with surface based process while in absorption there is involving of the whole volume of the matter [28].

By the phenomenon of the surface tension, adsorption is going to happen. All the bonding requirement like ionic covalent or metallic in bulk material to get attached to any other atom of biosorbate [29]. Adsorption process is mainly classified into two categories due to different species involved; those are

(1) Physisorption (Phenomenon of weak van der waal forces)

(2) Chemisorption (Phenomenon of covalent bonding results electrostatic attraction) [30].

2.2 Mechanism of adsorption

Biosorption mechanism possesses three steps. In an initial phase, the matter which is going to be absorbed that is biosorbate and substance which absorbs the liquid or gas i.e. absorbent. In the intermediate phase, the biosorbate is absorbed by the outer membrane of the absorbent according to higher pore size found on the surface. This follows the phenomenon of the surface tension. Finally, as higher the pore size, the more absorption capacity is seen. It is occurred due to the intermolecular interaction between an adsorbent and biosorbate [31, 32].

2.3 Adsorbate

Adsorbate is the substance which undergoes biosorption on the surface. During this event, charge transfer happens in between the biosorbate and metal which consequences the dipole moment formation [33]. The adhesion of atoms, ions, molecules and liquid or gas and dissolved solid particulates to the particular surface. As a result, the biosorbate film is formed on the adsorbent surface [34].

Malachite green is a traditionally used dye which is used to stain silk, leather, paper etc. The molecular formula of malachite green is $C_{23}H_{25}ClN_2$ and possesses the molecular weight of 364.91 g/mol. According to the chemical aspect, coloured cation is found in this dye. In the agricultural field, it is further used as bactericide, fungicide and parasiticide worldwide [35, 36].

The preparation of malachite green involves two steps:

1) The condensation of benzaldehyde and dimethyl amine helps in preparing leuco malachite green (LMG).

$C_6H_5CHO+2C_6H_5N\ (CH3)_2\ C_6H_5CH\ (C_6H_4N\ (CH_3)_2)_2 + H2O$

2) This colourless leuco compound's oxidation into the cation produces green pigment compound which is so called malachite.

$C_6H_5CH\ (C_6H_4N\ (CH_3)_2)_2 + HCl + ½\ O_2\ [C_6H5C\ (C_6H_4N\ (CH_3)_2)_2]\ Cl + H_2O$ [37, 38].

2.4 Removal method of dye

Table 1(a): Available Methods for treatment of dyes [39, 40].

Treatment Methodology	Stage of treatment	Type of Industry	Advantages	Limitations
I. Physical Methods				
***1.*Adsorption** a. Activated Carbon b. Bagasse c. Peat d. Wood chips	Pre/post treatment Pretreatment Pre treatment Pre treatment	Brewery/tannery/textile Sugar/Brewery Any industry Any industry	Bearing economical cost, good separation efficiency of Waste effluent recycling, No activation required for Good adsorption for colorants	Regeneration is expensive Hassel in disposal of Post- treatment effluent Requirement of lower surface area in huge quantity
2.Irradiation	Post treatment	Kraft mill, paper and pulp	Effective removal at low volumes	Requirement of dissolved Oxygen
3.Ion Exchange	Main treatment	Any industry	Low cost regeneration	Lesser applications
II. Chemical Methods				
***1.*Oxidation** a. Fenton's Regeneration b. Ozonation c. Electrochemical oxidation	Pre treatment Main treatment Post treatment	Textile Brewery/Distillery Kraftmill	Broad range of decolourizing Efficiency for both soluble as well as insoluble colours	Expensive and unsuitable for dispersed colours Cost -effective
***2.*Coagulation**	Pre treatment	Sugar/Pulp and paper	Low capital costs	Problems in dewatering and handling of sludge
III. Biological Methods				
1.Aerobic Process	Main treatment	Kraftmill/Tannery	Colour as well as COD removal	Longer detention time needed.
2.Anaerobic Process	Main treatment	Pulp and paper/sugar/distillery	For steam generation, Biogas is produced.	Longer phase of acclimatization
3.Single Cell(Fungal, Algae/Bacterial)	Post treatment	Any industry		It is unable to treat large volumes due to cost intensive

Table1 (b): Emerging technologies for treatment of dye [39, 40].

Treatment Methodology	**Stage of treatment**	**Type of Industry**	**Advantages**	**Limitations**
1.Advanced Oxidation Process	Main treatment	Distillery/Textile	Insurance of mineralization, enhances biodegradability	Expensive cost in processing
2.Membrane Filtration	Main treatment	Brewery/Tannery	Wider application for complex wastes	Dissolved particulates are not removed.
3. Photocatalysis	Post treatment	Any industry	Shorter detention times, a toxic and inexpensive	Most effective only for little amount of colorants
4.Engineered Wetland Systems	Pre/post treatment	Any industry which release large volumes of effluents	Can be operated on large volumes of water cost effectively	Hassel in managing during rainy season, high cost in installation,
5.Enzymatic Treatment	Post treatment Pre treatment	Any industry after biological treatment	Unaffected by shock loadings	Expensive cost in processing

The inference from literature review:

From the above theory, we can understand the basic concept of adsorption and types of adsorption. Moreover, there is the detailed description of how the process of adsorption is carried out on a physical and chemical surface and interacting forces. The substance which gets absorbed is known as biosobate and medium on which adsorption takes place is called biosorbent.

The equilibrium isotherm is analysed and the kinetic study to remove malachite green from aqueous solutions by adsorption has been studied. This is done by activated carbon. To analyse the effect of different parameters on a removal of dye adsorption studies were organised in batch form. The physical parameters that are taken into account are the time of contact, biosorbent dosage, pH, and the initial concentration of malachite green. It was estimated that the initial pH of the solution has strong effects on all the dye molecules and on the adsorbents present in the aqueous solution. The estimated time of contact was about to be 4 hours.

An agricultural waste, deoiled soya can also be used to removal malachite green and its recovery. Techniques of batch adsorption can also be utilised as a primary study by considering the deoiled soya' concentration, time of contact, sieve size etc.

A bentonite has also been used to study on removal of malachite green and the physical parameter of biosorption has been calculated. Till equilibrium was reached, the dye removal increases with increasing the time of contact and initial dye's concentration and also the biosorption ability of used adsorbent has not any effect of initial pH ranging from 3-11.

The fibre of oil palm trunk was estimated to remove malachite green dye from solution" where all variables which were utilising were initial dye' concentration, time of contact for adsorption and pH. The Langmuir and the Freundlich isotherm examined the equilibrium data adsorption. The increase in dye concentration results in a increase the pore diffusion coefficient.

Neem sawdust can also be utilised for removal of malachite green from solution. Some conditions of the experiment like time are important for efficient agitation, the concentration of dye, biosorbent dosage, pH of the solution to verify "the ability of sawdust of neem to remove malachite green dye from aqueous water". The decrease in dye concentration and biosorbent dosage results in an increase in percentage removal efficiency of dye.

Chapter 3

Materials & Methods

3.1 Materials

3.1.1 Instruments

1. Incubator shaker
2. Analytical balance
3. pH meter
4. Micro Centrifuge
5. Spectrophotometer
6. SEM
7. FTIR
8. XRD

3.2 Methods

3.2.1 Preparation of Adsorbent

Papaya wood saw dust

Papaya wood was drawn from the fallen trees' felled trunk. The trunk was debarked and then cut into small pieces, dipped for 30 min in boiling water. Then it was washed with tap water, and left for 2–3 h in distilled water, changed 3–4 times consecutively. The cleaned wood pieces were ground into small fine particles by electric-grinder. These ground particles are sieved through sieves (having different pore sizes) to obtain the desired fibres. Fibres with different sizes i.e. <425 microns, 425-250 micron, 250-150 micron, 150-125 micron, 125-106 micron, <106 microns were obtained. We needed the sample having particle size 100-200 microns out of these samples for better observation. So, the sample with the particle size in the range 150-125 micron was selected.

Banana peel saw dust

Banana peel was collected from the marketplace. It was then washed thoroughly about 2-3 times using tap water. It was the dried in sunlight for 2 days. The dried peel was ground into small particles. These ground particles are sieved through sieves (having different pore sizes) to obtain the desired fibres. The sample with the particle size in the range 150-125 micron was selected.

Bael shell saw dust

Bael fruits were collected from fallen bael tree. Then shell was separated from the bael fruits and washed the shells from tap water to remove the fruit part. Then shell was ground into the small shell and dried in sunlight for 2 days. Dried shell was again ground into small particles and then it was sieved through sieves. The sample with the particle size in the range 150-125 micron was selected.

3.2.2 Experimental Procedure

Study of pH

Nine concentrations of working solutions were each of 10mg/l made. These were kept at different pH starting from 2 to ending at 10 by adding 0.1N HCl or NaOH drops.

0.1 gram of biosorbent matter was added to each and kept in incubating shaker at room temperature as well as at 120 revolutions per minute for 2 hours. The solution mixtures were taken after 2 hours and then centrifuged and analysed in UV-Spectrophotometer.

Study of biosorbent Dosage

Standard solutions of a colour of 10 mg/l were prepared once again from the stock solution. pH of all solution was adjusted at 10 (for papaya sawdust absorbent), 7 (for banana peel) and 8 (for bael shell). To every solution, the adsorbent was dropped but in a varied range from 0.02 to 0.18 gram respectively. These solution mixtures containing the various quantity of biosorbent dose were shaked, centrifuged and then analysed in UV-Spectrophotometer.

Study of initial dye concentration

Different concentrations of working solutions having ranges 10-50mg/L were prepared. To all these solutions, 0.06 gram (papaya sawdust)/ 0.1 gram (banana peel)/ 0.12 gram (bael shell) was mixed as an adsorbent. The initial pH of the solutions was retained at 10 (papaya sawdust)/ 7 (banana peel)/ 8 (bael shell).

Study of temperature

A 50 ml solution mixture of conc. 10 mg/l was made from the stock solution by dilution. To all of three solution mixtures, 0.06 gram (papaya sawdust)/ 0.1 gram (banana peel) / 0.12 gram (bael shell) of adsorbent was mixed and they were retained at pH 10(papaya)/ pH 7 (banana peel) / pH 8 (bael shell). The solutions were put into shaking incubator at 120 revolutions per minute for 2 hours but at different temperatures of 30°C, 40°C and 50°C. After finishing off a couple of hours, they were placed out of the incubating shaker, kept in centrifuge device for 10minutes and then finally analysed in the UV-Spectrophotometer method. This process was done for the concentration of 20 mg/l, 30 mg/l, 40mg/l and 50mg/l.

After all of this investigation of various factors, the quantity adsorbed is estimated as:

Qe= (Co-Ce)/(x)Where,

Qe = Adsorbed quantity of dye per unit mass of adsorbent matter (mg/g).

C_o= Initial concentration of dye (mg/L).

Ce= Final concentration of dye (mg/L).

X = Biosorbent dosage (g/L). [40, 41]

3.2.3 Adsorption Isotherms

An isotherm of adsorption is proposed by specific constant numbers which exhibits the characteristics of surface and the adsorbent matter's affinity and could further be deployed to differentiate the biosorptive capacity of the biosorbent for different pollutants and wastes. The comfort model at persistent temperature for this biosorption process is Langmuir or Freundlich model [42].

Langmuir Isotherm:

Assumptions of Langmuir Isotherm are:

1) The biosorption on biosorbent’s surface is considered to be consistent, i.e., every sites found on adsorbent are showing similar adsorption.

2) The adsorbed materials don’t show interaction force between them.

3) Same mechanism is applied for all kind of adsorption process.

4) A single monolayer is considered to surround on the site for optimum biosorption, that is molecular particles of biosorbate solution mixture do not get deposited on another molecular

matters of itself which hitherto get into surface. Meanwhile, other molecules found on the rest of surface suitable for the biosorption.

$Ce/Qe=1/(Qm.K_L)+Ce/Qm$

Ce- Dye's concentration at equilibrium

*Q*e- Adsorbate volume adsorbed per gram of adsorbent at equilibrium;

Qm- Langmuir constants which is related to biosorption capacity

K_L- Langmuir constants which is associated with biosorption energy

The Langmuir-constants K_L and Qm can obtained by the intercept and slope of plot between Ce/Qe *vs* Ce [43, 44].

Freundlich Isotherm:

Theory of Freundlich isotherm demonstrates the quantitative relation analysis i.e. the ratio of the biosorbate amount solution got into a biosorbent mass matter to the concentration of biosorbate in the solution [45, 46]. This is practicable to biosorb on different surfaces' site and can be understood by linear form equation given as:

$Log\ Qe=Log\ K_F+1/n_F\ (Log\ Ce)$ [47].

Qe - Absorbed amount of solute.

K_F - Freundlich constant which is related to biosorption capacity.

n_F - Freundlich constant which is related to biosorption intensity.

Ce - Solute concentration at equilibrium.

3.3 Characteristics of biosorbent

3.3.1 Fourier transforms infrared spectroscopy (FTIR) Analysis

It is a method which is applied to get an infrared spectrum drawn of absorption or emission of a liquid, solid, or gas. This spectrometer at a time collects a wide spectral range and then estimates high spectral resolution data. This type of spectrum is a graph which has wavelength or frequency along the X-axis and percent transmittance along the Y axis. After observing the peak between specific frequencies i.e. band or gap, type of the functional site may be obtained by looking given table.

3.3.2 Scanning electron microscopy (SEM)

Scanning Electron Microscope first scans the surface of solid by an electron beam and then projects images on the screen of a computer. The beam of electron bombards the atoms present on a surface of the sample which produces different signals. Those signals are recognised by the electron detector. Those signals contain data of the surface structure and composition of the sample. Samples possess appropriate size are used since those have to be taken in a chamber which only suitable for specific size samples.

3.3.3 X-ray diffraction (XRD)

X-ray diffraction is nowadays a promising method for the study of atom spacing and structure of crystals. A cathode ray tube generates x-rays, then it goes on filtration to collimate to concentrate, produce monochromatic radiation and directs toward the sample. The incident rays' interaction with the sample generates interference of constructive (and a ray of diffraction) when Bragg's Law is satisfied by environmental criteria. Through a range of 2θ angles, the sample is scanned and all possible directions of diffraction of the lattice bound to be attained due to the powdered material's random orientation.

Chapter 4

Results and Discussion

4.1 Characteristics of biosorbents:

FTIR is done to estimate the important parameters i.e. functional groups that influence and determine the biosorption of dye from wastewater by biosorbent materials. Here, this is done for papaya wood, banana peel and bael shell. The grounded biomass obtained was sieved using siever. The desired sieved particle size 150-200 microns were used for carrying out FTIR analysis. The result of FTIR analysis gives which functional groups are present in various biosorbent materials which are used. These functional groups are involved in the mechanism of the removal of dye.

FTIR Analysis of raw papaya wood sample

Figure 2(a) and figure 2(b) gives the spectra of the FTIR of the papaya wood sample before biosorption and after adsorption and table 2(a) gives the prediction of compounds present in the sample before adsorption and after adsorption; which is obtained by the peaks between following band.

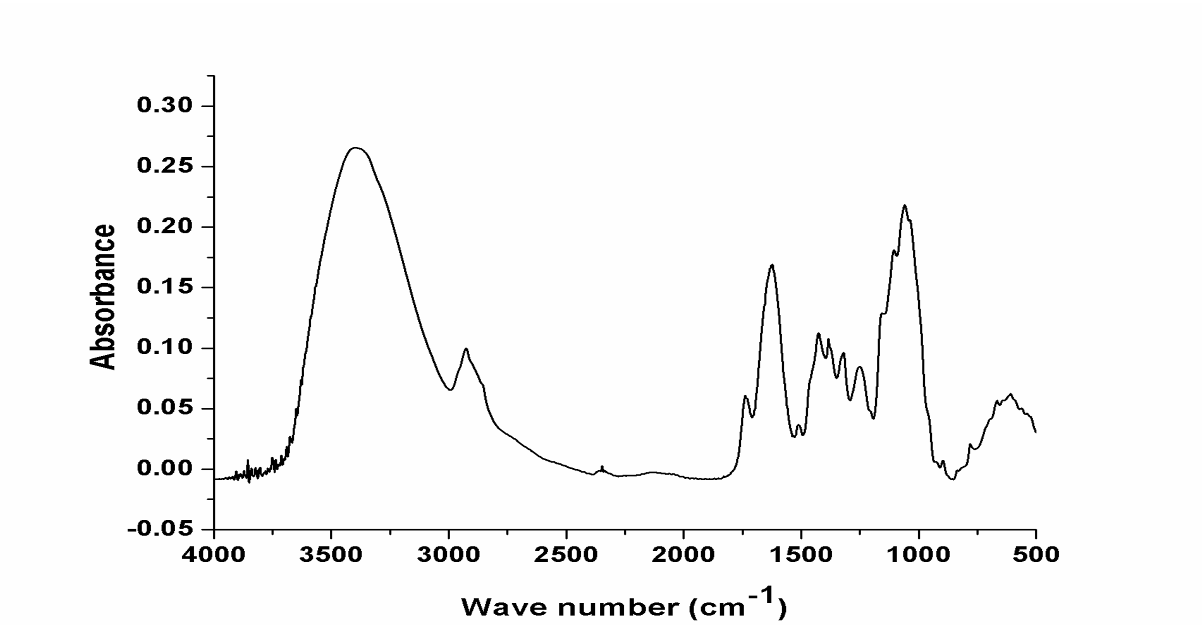

Figure 2(a): FTIR image of papaya wood before biosorption of malachite green.

FTIR Analysis of papaya wood sample with Malachite green

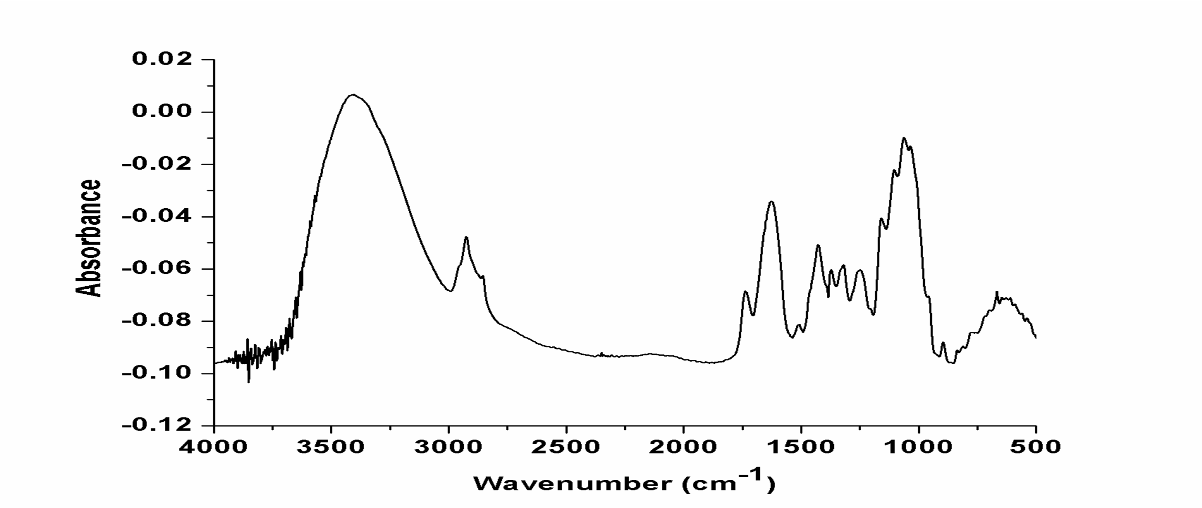

Figure 2(b): FTIR image of papaya wood after biosorption of malachite green.

Table 2(a): Prediction of compounds that present in papaya wood biosorbent

Wave-number(cm-1)	**Functional group**	**Compounds**
3402	O-H Stretch	Carboxylic Acid
2925	N-H Stretch	Amine
1737	C=O Stretch	Ketone
162	C=C Bending	Aromatic
1510	N=O (aromatic)	Nitro group

To find out the functional groups of papaya wood FT-IR spectra in the range of 500–4000/cm for papaya wood before and after malachite green added were determined and shown in Fig. 2(a) and 2(b). The results of FT-IR spectra of the papaya wood in native form and after malachite green biosorption are depicted in Table 2(a). Significant shift of biosorption peak frequencies 3402 and 2925/cm reflects dye binding or without dye binding with the Carboxylic/OH stretching and N–H stretching. The band 1737 and 1382.52/cm was assigned to the stretching vibrations of C=O stretch from the lignin structure of papaya wood has been observed. The peaks appearing in the region 1510/cm and 162/cm represent C=C bending and N=O. Papaya wood sample is rich in oxygen functional groups. Formation of such functional groups enhances the biosorption capacity.

FTIR Analysis of banana peel raw sample

Figure 2(c) and 2(d) gives the spectra of the FTIR of the banana peel sample before biosorption and after adsorption. Table 2(b) gives the prediction of compounds present in the sample before adsorption and after adsorption; which is obtained by the peaks between following bands.

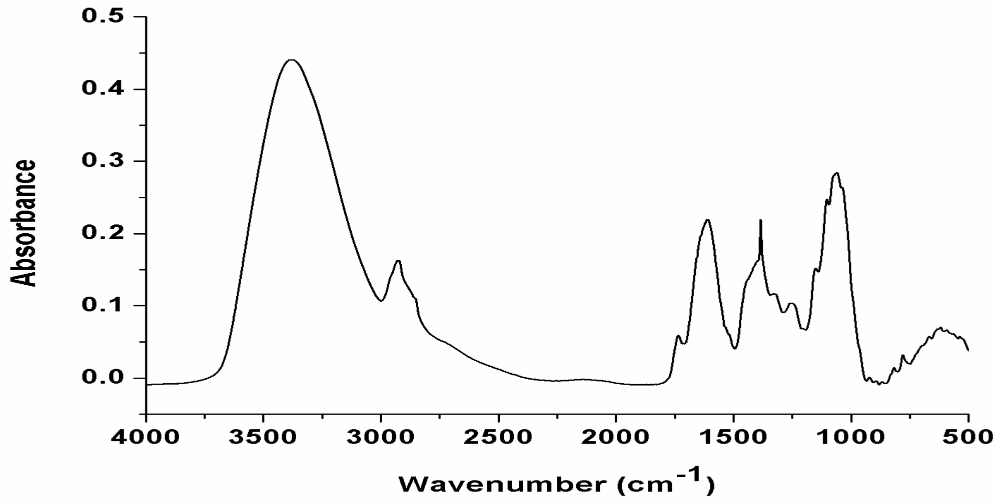

Figure 2(c): FTIR image of banana peel before adsorption of malachite green.

FTIR Analysis of banana peel sample with malachite green

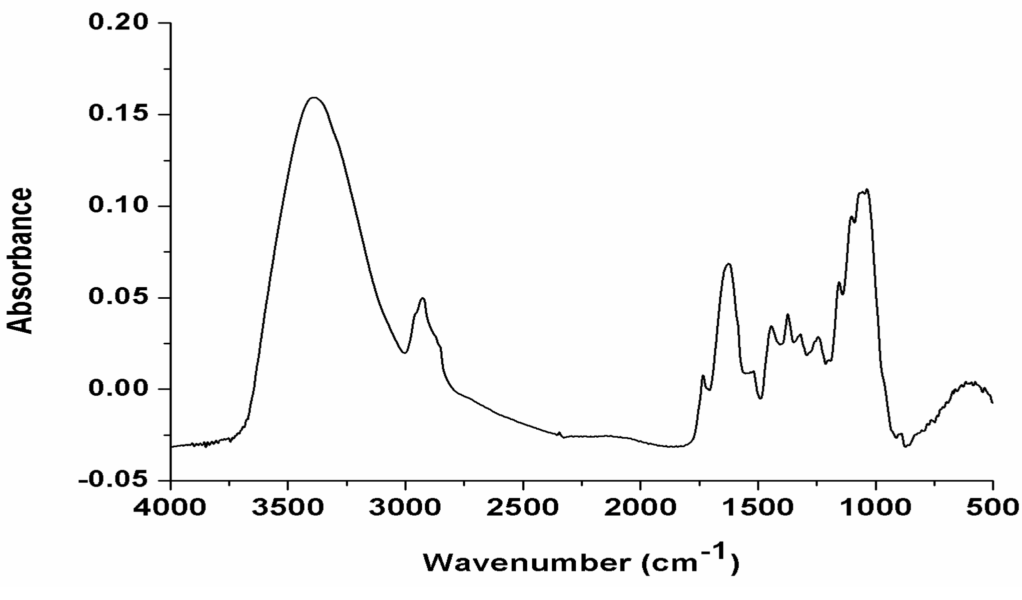

Figure 2(d): FTIR image of banana peel after adsorption of malachite green.

Table 2 (b): Prediction of compounds present in the banana peel sample

Wave-number (cm-1)	**Functional group**
3380	N-H
2926	C-H Stretch
1753	C-O-O-R
1612	C=C

The range of 500–4000/cm for banana peel before and after malachite green loaded is observed to obtain the main functional groups of banana peel FT-IR spectra and shown in Fig. 2(c– d). The results of FT-IR spectra of the banana peel in native form and after malachite green biosorption are shown in Table 3(a). Significant shift of biosorption peak frequencies 3360 reflects dye binding or without dye binding with N–H stretching. The band 1595 and 1331/cm was assigned to presence of symmetric nitro and symmetric nitro from the lignin structure of banana peel are observed. The peaks which present in the region 1247/cm and 1034/cm represent alkoxy alcohol and cayno group. Papaya wood sample is rich in oxygen functional groups. Formation of such functional groups enhances the biosorption capacity.

FTIR Analysis of bael shell raw sample

Figure 2(e) and 2(f) gives the spectra of the FTIR of the bael shell sample before biosorption and after adsorption. Table 2(c) gives the prediction of compounds present in the sample before adsorption and after adsorption; which is obtained by the peaks between following band.

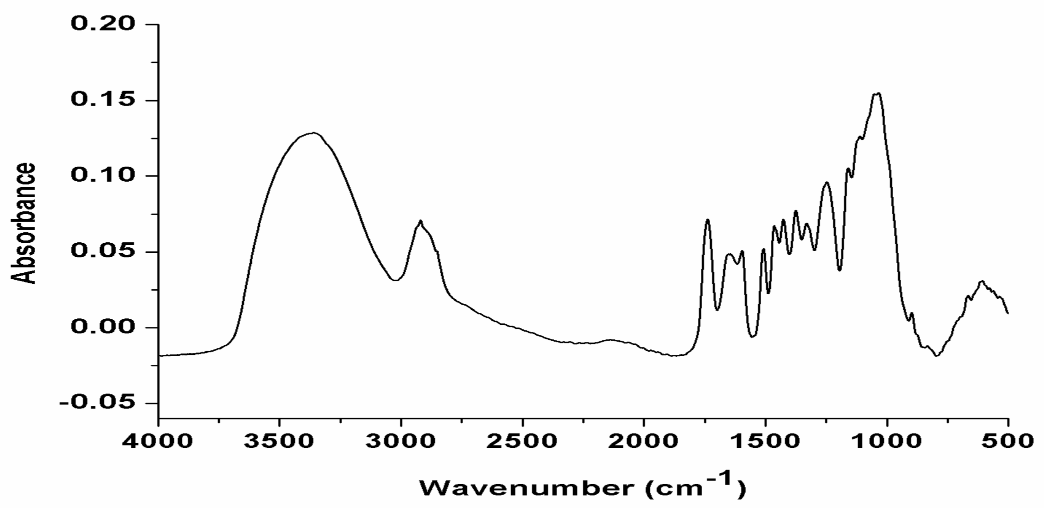

Figure 2(e): FTIR image of bael shell before adsorption of malachite green.

FTIR Analysis of bael shell sample with Malachite green

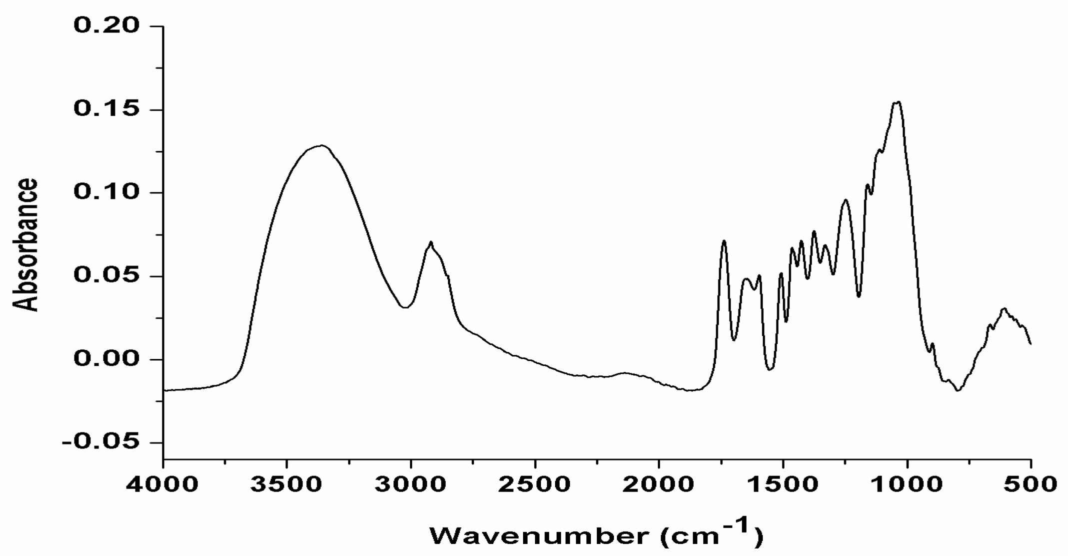

Figure 2(f): FTIR image of bael shell after adsorption of malachite green.

Table 2(c): Prediction of compounds present in the bael shell sample

Wave-number(cm-1)	**Functional group**	**Compounds**
3360	N-H	Amine
1595	N=O	Nitro (Asymmetric)
1331	N=O	Nitro (Symmetric)
1247	R-O-R	Alkoxy alkohol
1034	C-N	Cyano

The functional groups present in bael shell sample are: N-H, N=O, R-O-R, C-N. These are obtained from the result of FTIR analysis.

To analyse the functional groups of bael shell FT-IR spectra having range of 500–4000/cm for bael shell before and after malachite green loaded were analyzed and shown in Fig. 2(e–f). The results of FT-IR spectra of the bael shell are shown in Table 2(c). Significant shift of biosorption peak frequencies 3360 and 1595/cm reflects dye binding or without dye binding with the amine group and asymmetric nitro group. The band 1331 and 1247/cm are presenting the stretching vibrations of symmetric nitro group and alkoxy alcohol.

4.1.2 XRD plot of Papaya wood, Banana peel and bael shell:

The XRD OF papaya wood, banana peel and bael shell is shown in the figure 3. The XRD is used to analyse the structural features of biosobents, whether they are crystalline or amorphous in nature. The sieved biosorbent samples of size 150-200 microns is used to perform XRD.

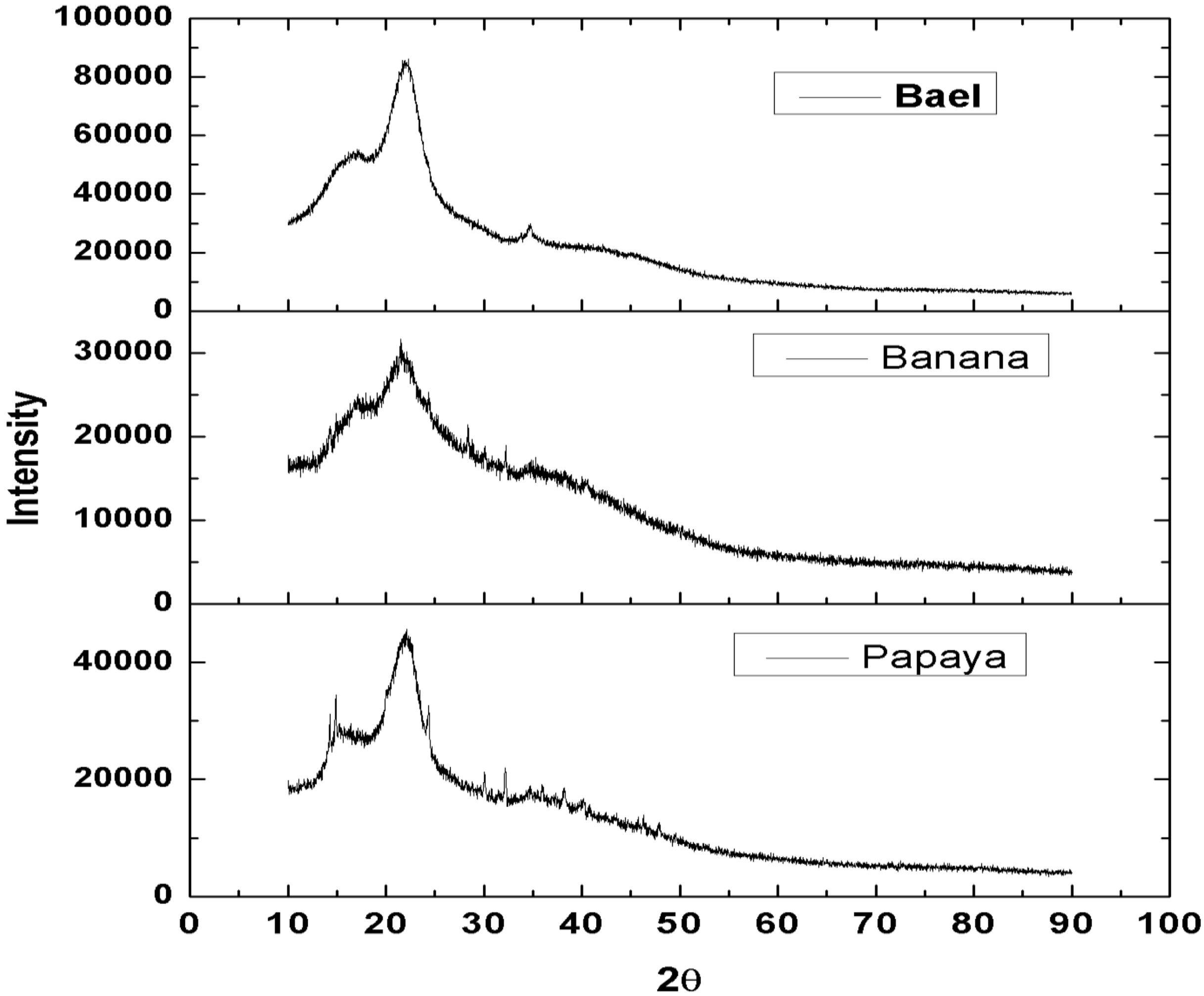

Figure 3: XRD of papaya wood, banana peel and bael shell.

The XRD analysis of solid digestates from all feedstock clearly showed the amorphous nature of the by-products. Some other minor peaks of biosorbents can be attributed to presence of some crystal forms. It is observed that the result showed a broad peak at 2 theta values of around 20–30°.

4.1.3 SEM image (papaya wood, banana peel and bael shell sample)

The SEM images of all biosorbent are shown in the figure 4. The images show the biosorbents have significant pore numbers for dye's biosorption onto them. Pores that present within the biosorbent are heterogeneous. They have a highly porous structure.

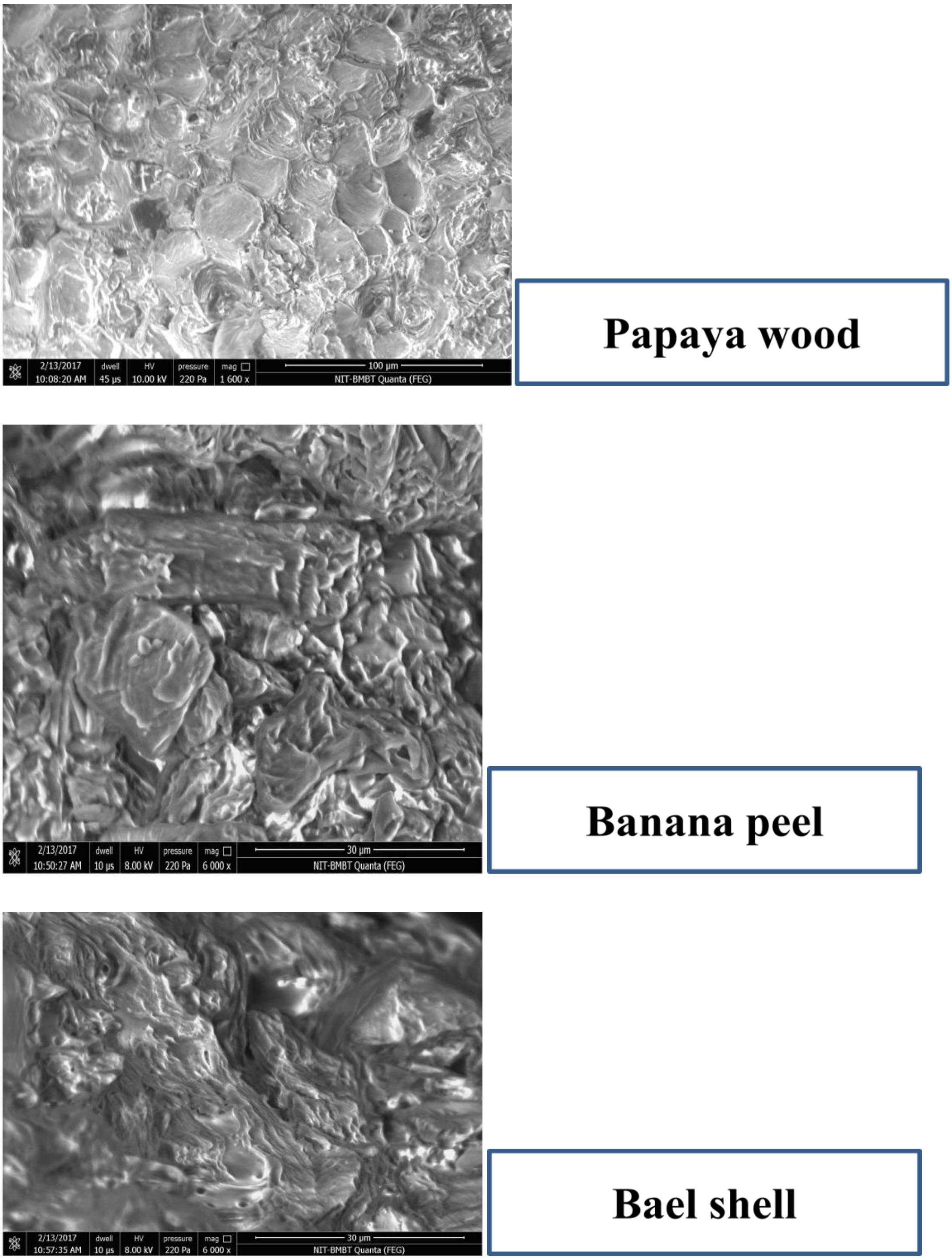

Figure 4: SEM image of raw form of papaya wood, banana peel and bael shell.

4.2 Adsorption study

4.2.1 Effect of pH

The pH of the aqueous solution is one of the major controlling parameters in process of the malachite green dye biosorption. The effect different pH ranging from 2 to 10 at dye concentration of 10 mg/L on papaya wood was studied. The plot of dye removal efficiency for different pH is shown in Figure 5(a).

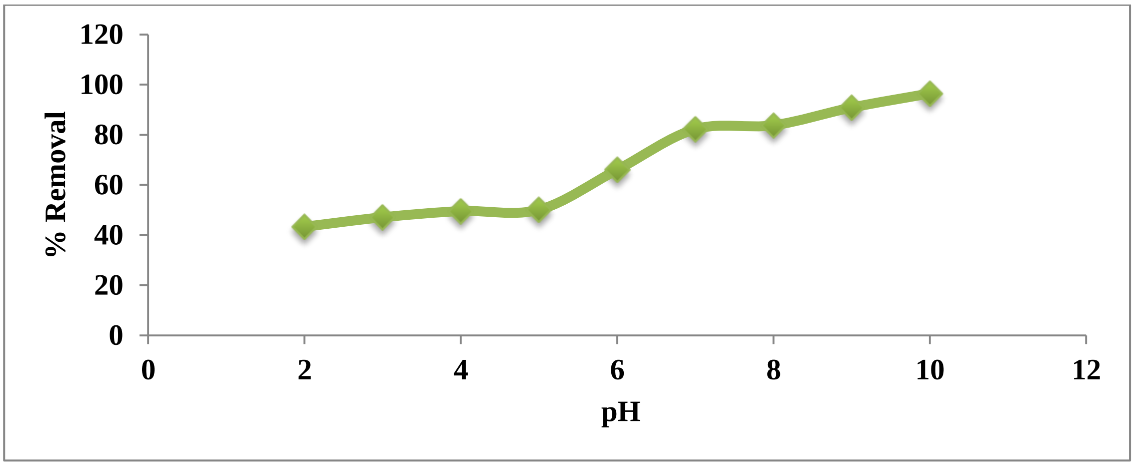

Figure 5(a): Effect of pH on % removal of malachite green by papaya wood biosorbent.

The effect different pH having range 2 to 10 at an initial dye concentration of 10 mg/L on banana peel was studied. The plot of dye removal efficiency for different pH for banana peel is shown in Figure 5(b).

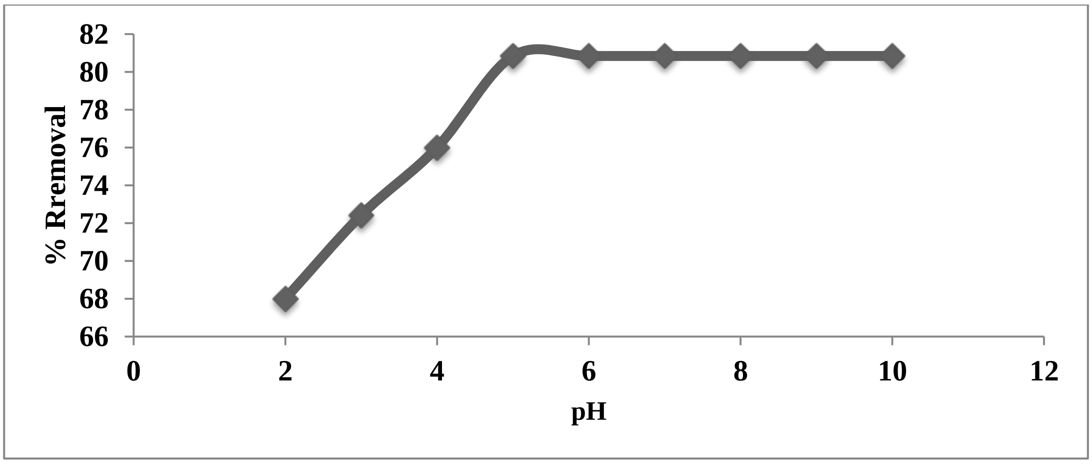

Figure 5(b): Effect of pH on % removal of malachite green by banana peel biosorbent.

The effect different pH ranging from 2 to 10 at an initial dye concentration of 10 mg/L on bael shell is studied. The plot of dye removal efficiency for different pH for bael shell was shown in Figure 5(c).

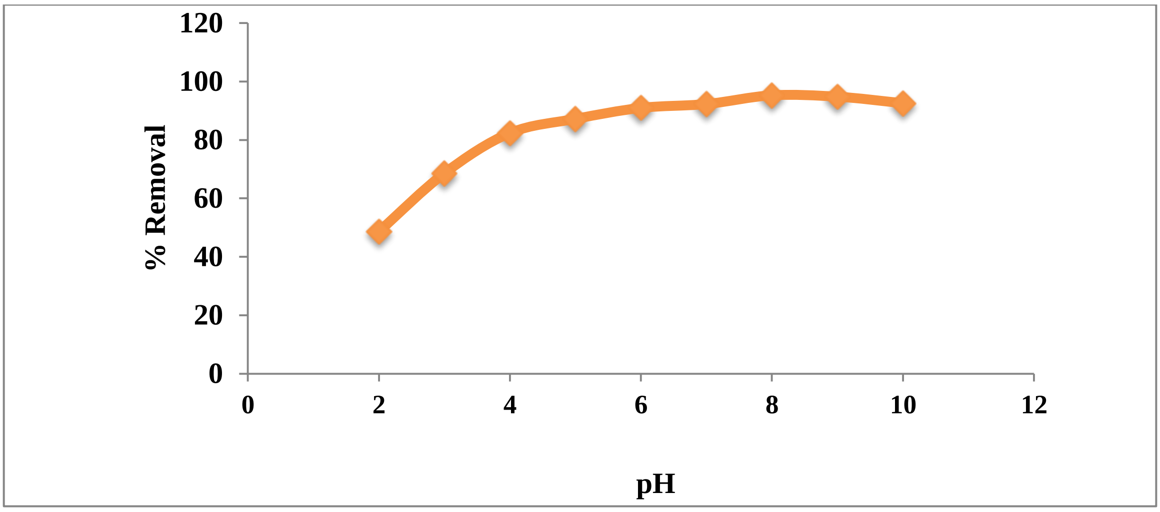

Figure 5(c): Effect of pH on % removal of malachite green by bael shell biosorbent.

The biosorbent's surface characteristics and the degree of ionisation of molecules of dye has influenced by the initial pH of dye solution. Different samples were taken to observe the impression of initial pH on the quantity of dye. The samples are papaya wood, banana peel and bael shell. The results are illustrated in the graph and the clue from the graph that in the pH range 7-10 the removal efficiency of dye is high in case of all biosorbent. Due to the interaction forces between the positively charged dyes cations with functional group sites on the surface biosorbent, the higher biosorption is at very basic media. On the contrary, the adsorption boosts its rate at higher pH values.

4.2.2 Effect of dosage

The removal of malachite green was studied by varying the papaya wood dosage ranging from 0.02 to 0.18 gram in 10 mg/l initial dye concentration, temperature (30°C), pH (10) and agitation speed (120 rpm) constant for 120 min. The plot of dye removal efficiency for different papaya wood dosage is shown in Figure 6 (a).

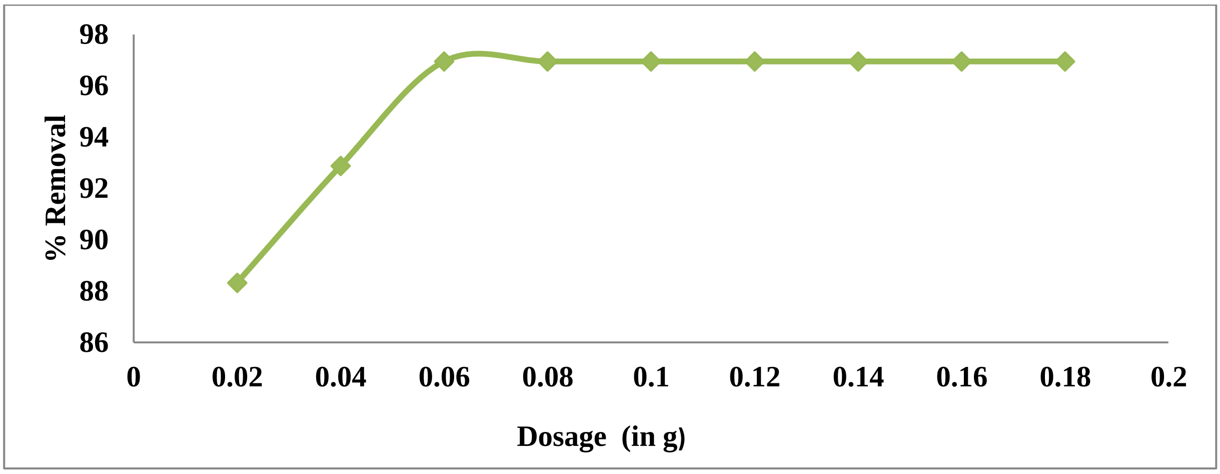

Figure 6(a): Effect of dosage on % removal of malachite green by papaya wood.

The removal of malachite green was studied by varying the banana peel dosage ranging from 0.02 to 0.18 gram in 10mg/l initial dye concentration, temperature (30°C), pH (7) and agitation speed (120 rpm) constant for 120 min. The plot of dye removal efficiency for different banana peel dosage is shown in Figure 6 (b).

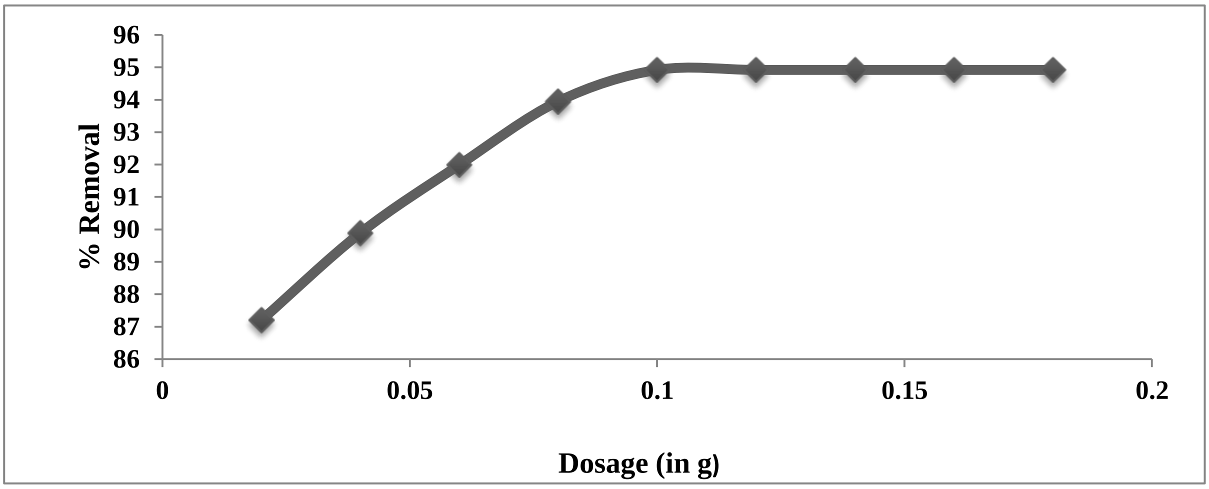

Figure 6(b): Effect of dosage on % removal of malachite green by banana peel biosorbent.

The removal of malachite green was studied by varying the bael shell dosage ranging from 0.02 to 0.18 gram in 10mg/l initial dye concentration, temperature (30°C), pH (8) and agitation speed (120 rpm) constant for 120 min. The plot of dye removal efficiency for different bael shell dosage is shown in Figure 6 (c).

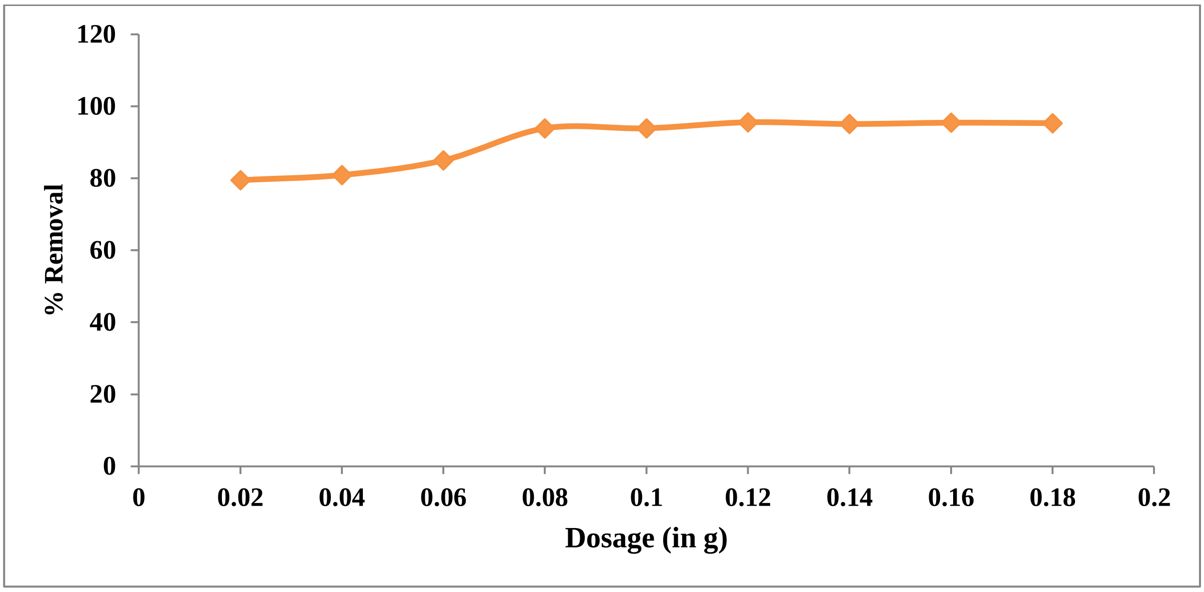

Figure 6(c): Effect of dosage on % removal of malachite green by bael shell biosorbent.

Graphs for all biosorbent elucidate that the separated of dye's percentage rises while increasing in the biosorbent dosage. As the biosorbent dosage added, a substantial enhancement in suitable biosorption regions generated in a high percentage efficiency of biosorption. Furthermore, the competition of dye particulates for suitable biosorption regions, further agglomeration of the biosorbent particulates, and a boosting in length of diffusion path can be the causes for the reduction in uptake of dye at higher biosorbent magnitude of dosage. The number of active regions on the surface of biosorbent was raised by adding the dosage, co-sequencing in the boosting of dye species removal.

4.2.3 Effect of initial Malachite green (MG) concentration

The removal of malachite green was studied by varying the concentration of dye ranging from 10 mg/l to 50 mg/l in 0.06 gram dosage of papaya wood, temperature (30°C), pH (10) and agitation speed (120 rpm) constant for 120 min. The plot of dye removal efficiency with varying dye concentration for papaya wood is shown in Figure 7 (a).

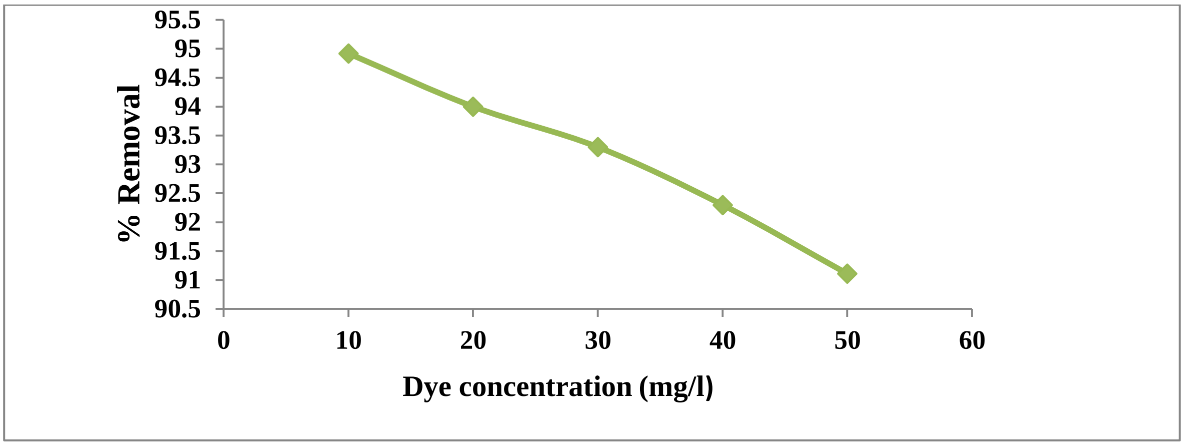

Figure 7(a): Effect of initial dye concentration on the removal of malachite green by papaya wood biosorbent.

The removal of malachite green was studied by varying the concentration of dye ranging from 10 mg/l to 50 mg/l in 0.1 gram dosage of banana peel, temperature (30°C), pH (7) and agitation speed (120 rpm) constant for 120 min. The plot of dye removal efficiency with varying dye concentration for banana peel is shown in Figure 7 (b).

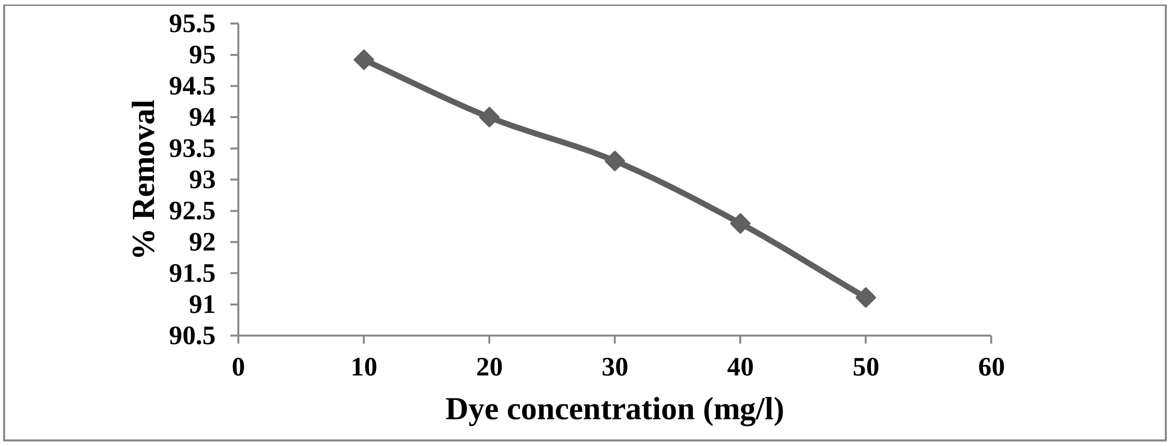

Figure 7(b): Effect of initial dye concentration on the removal of malachite green by banana peel biosorbent.

The removal of malachite green was studied by varying the concentration of dye ranging from 10 mg/l to 50 mg/l in 0.12 gram dosage of papaya wood, temperature (30°C), pH (8) and agitation speed (120 rpm) constant for 120 min. The plot of dye removal efficiency with varying dye concentration for bael shell is shown in Figure 7 (c).

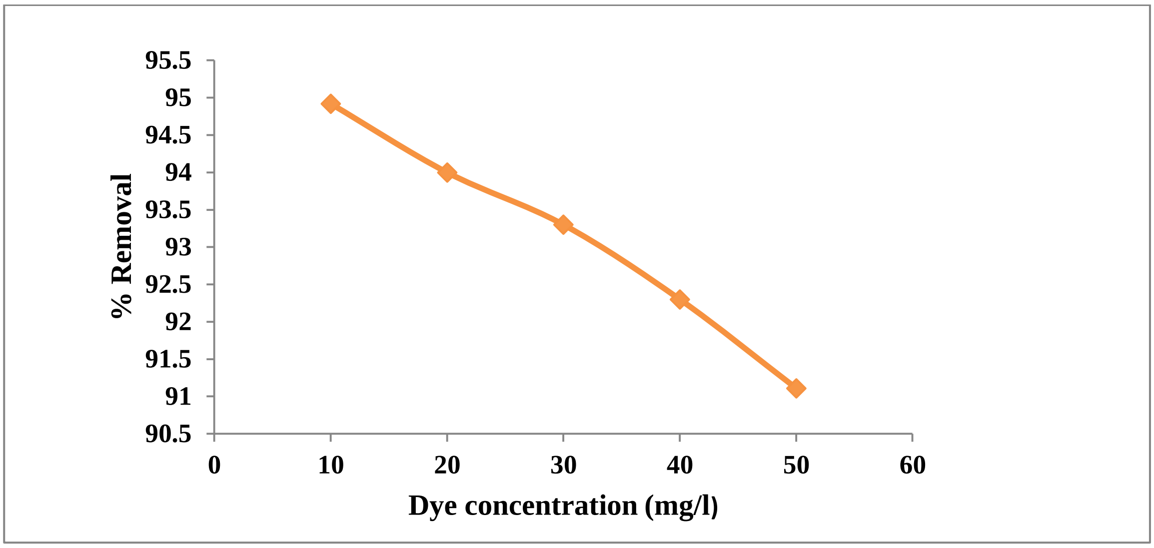

Figure 7(c): Effect of initial dye concentration on the removal of malachite green by bael shell biosorbent

The dye's concentration has a perceptible influence on its partition from liquid solution. In the initial concentration range of 10-50 mgL-1, the effect of concentration of malachite green dye on the efficiency of biosorption was also observed as shown in figure. The dye removal efficiency reduces with increasing in the initial concentration of dye. Biosorbent has a some limited numbers of active regions, which turns saturated at a certain concentration level. However, the concentration will inversely affect on the frequency of biosorption because of the limited biosorption regions found for the uptake of cationic dye particles. Initially in the solution, the dye’s concentration is higher, then active sites on surface of biosorbent are covered by numerous amounts of colour molecules which have more tendencies for biosorption.

4.2.4 Effect of initial dye concentration on biosorption capacity of biosorbents

Figure 8(a) shows the effect of initial dye concentration on biosorption capacity of papaya wood. The increase in biosorption capacity of the papaya wood with increasing dye concentration is due to collision between dye ions and papaya wood increased driving force of the concentration gradient.

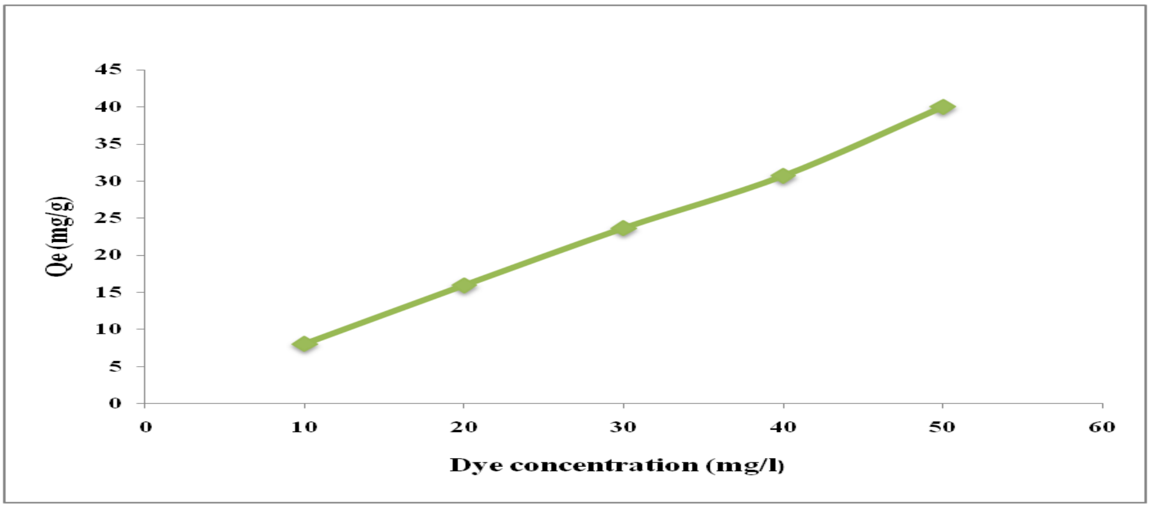

Figure 8(a): Effect of initial dye concentration on the biosorption capacity of papaya wood

The biosoption capacity of banana peel is studied by varying the concentration of dye ranging from 10 mg/l to 50 mg/l which is shown in the figure 8(b).

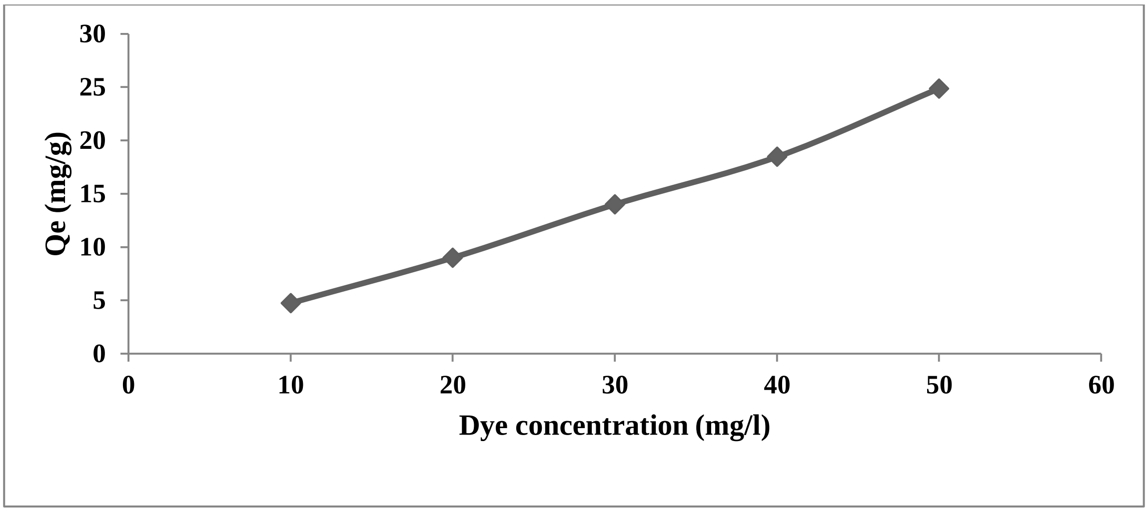

Figure 8(b): Effect of initial dye concentration on biosorption capacity of malachite green by banana peel biosorbent.

The biosorption capacity of bael shelll is studied by varying the concentration of dye ranging from 10 mg/l to 50 mg/l which is shown in the figure 8(c). Increase in initial dye concentration results in an increase in biosorption capacity.

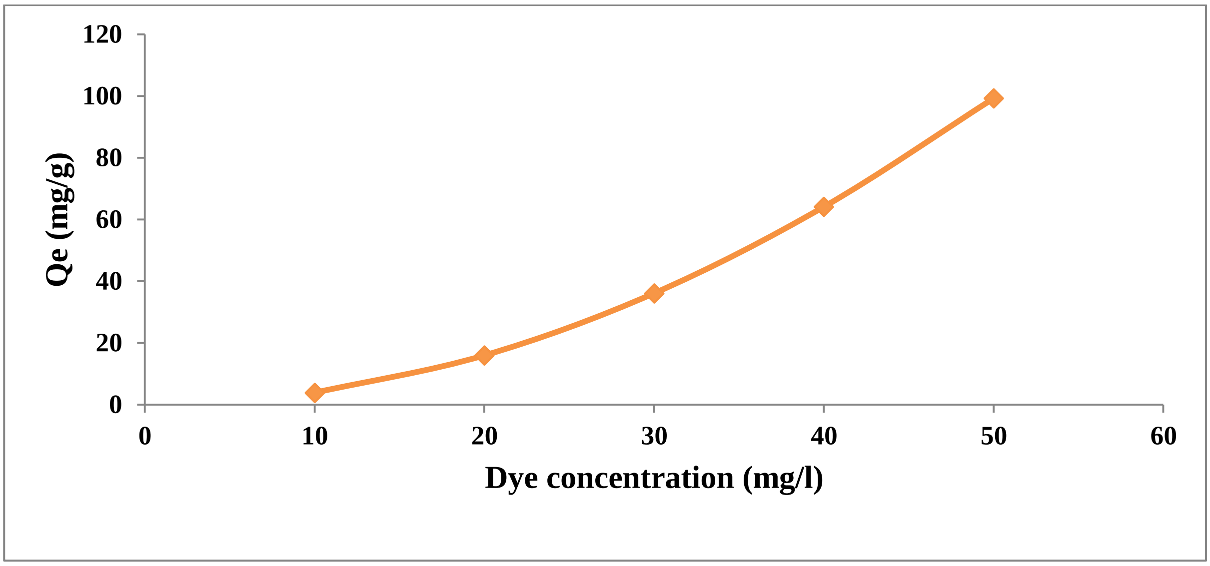

Figure 8(c): Effect of initial dye concentration on biosorption capacity of malachite green by bael shell biosorbent.

The rate of biosorption is a function property of the initial conc. of the biosorbate, which is considered it as an important factor to be taken for efficient biosorption. Raising the initial concentration of the dye induces in a boosting in the biosorption efficiency because it gives a driving force to get across all resistances related to mass transfer of dye particulates between the aqueous solution and solid phase particle. Biosorption efficiency will rise with the adding of initial concentration of dye mainly due to the enhancement in the mass transfer from the concentration gradient.

4.2.5 Effect of temperature on removal of malachite green

Temperature is one of the major controlling parameters in process of the malachite green dye biosorption. The biosorption experiments is conducted in the temperature range of 30°C-50°C at dye concentration 10 mg/l, at pH 10 and contact time of 120 min. The maximum dye removal capacity of papaya wood is observed at 50°C and results is shown in the Figure 9(a).

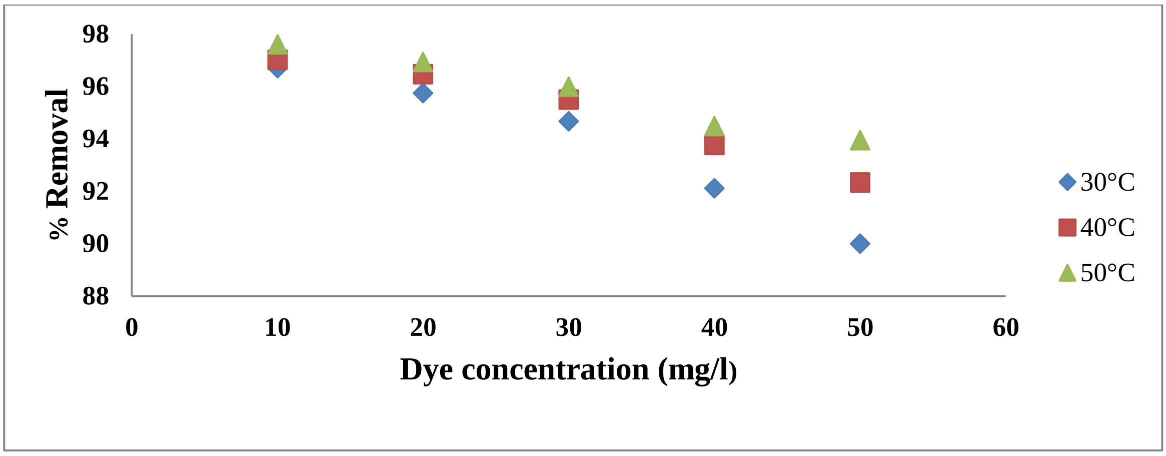

Figure 9(a): Effect of temperature on the removal of malachite green dye by papaya wood adsorbent.

The biosorption experiments is conducted in the temperature range of 30°C-50°C at dye concentration 10 mg/l, at pH 7 and contact time of 120 min. The maximum dye removal capacity of banana peel is observed at 50°C and result is shown in the Figure 9(b).

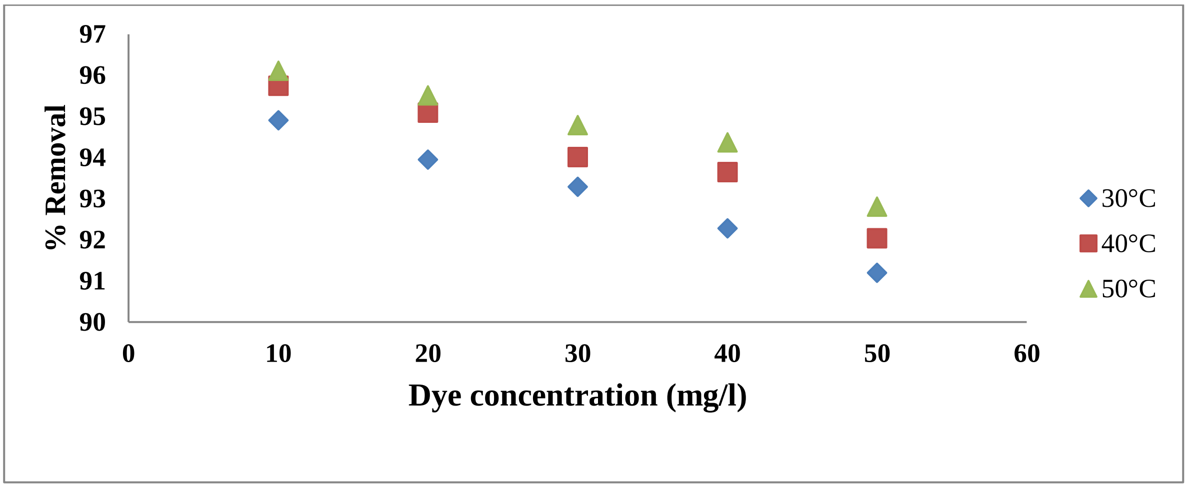

Figure 9(b): Effect of temperature on the removal of malachite green dye by banana peel biosorbent

The biosorption experiments is conducted in the temperature range of 30°C-50°C at dye concentration 10 mg/l, at pH 8 and contact time of 120 min. The maximum dye removal capacity of bael shell is observed at 50°C and result is shown in the Figure 9(c).

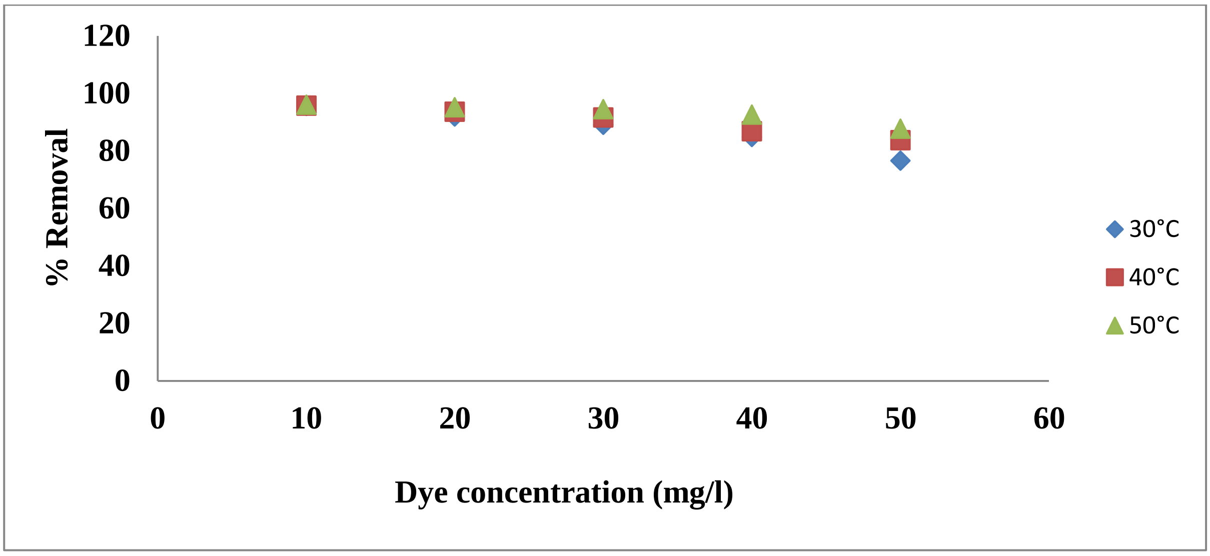

Figure 9(c): Effect of temperature on the removal of malachite green dye by bael shell biosorbent

Temperature is a noticeable controlling element uses of biosorbent for the dye separation process. Above graph demonstrates the biosorption of green dye by papaya wood, banana peel and bael shell at various temperatures. The temperature influences the dye's biosorption capacity certainly that is the percentage separation of dye reduces on rising the system's temperature. An increment of temperature influences percentage removal of malachite green because with the rise in temperature increases pore volume of the biosorbent and also it increases rate diffusion of dye molecules within pores of the biosorbent particles. This trend can be accredited to the certitude that the chemically interaction forces occurring between green dye and the biosorbent is endothermic by nature.

4.3 Adsorption isotherms

4.3.1 Langmuir Isotherm

The equilibrium data has been linearized using the Langmuir equation and is plotted between Ce/qe versus Ce for papaya wood in shown in figure 10(a).

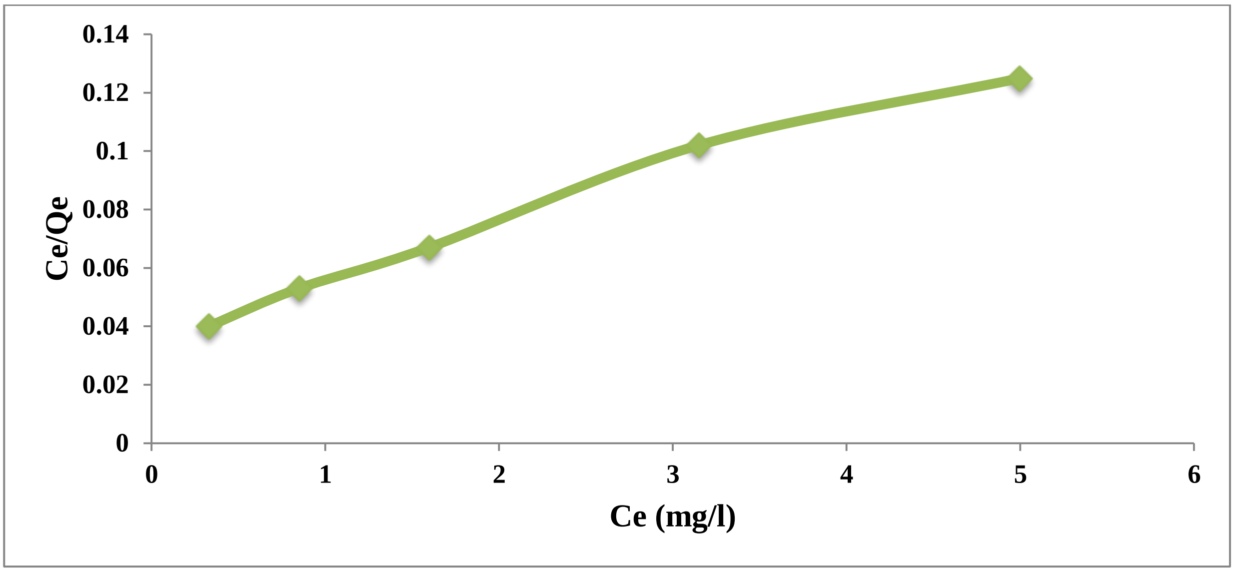

Figure 10(a): Langmuir adsorption isotherm for malachite green for papaya wood.

The equilibrium data has been linearized using the Langmuir equation and was plotted between Ce/qe versus Ce for banana peel is shown in the figure 10(b).

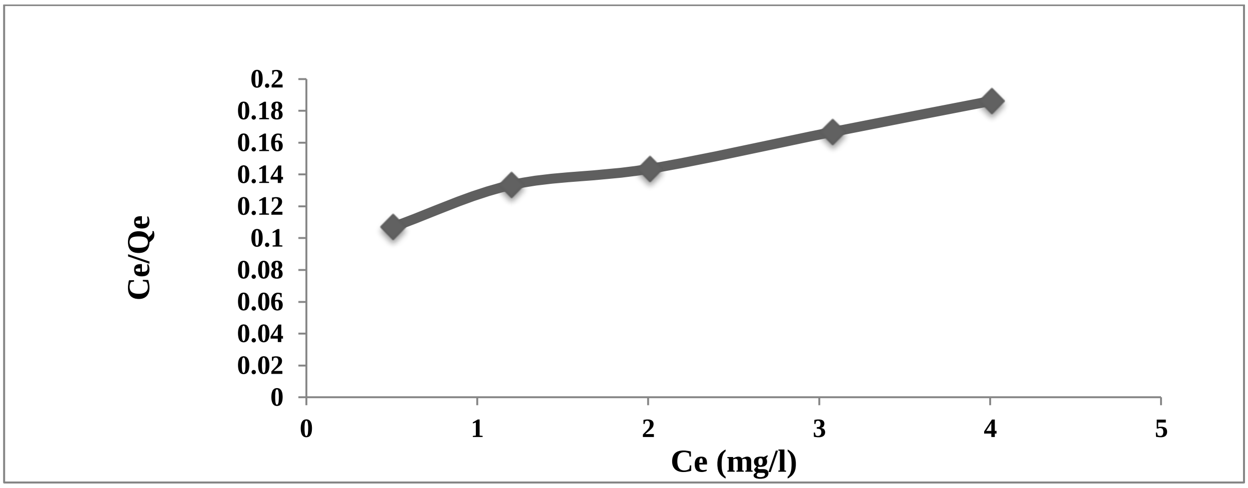

Figure 10(b): Langmuir adsorption isotherm for malachite green for banana peel.

The equilibrium data has been linearized using the Langmuir equation and was plotted between Ce/qe versus Ce for bael shell is shown in the figure 10(c).

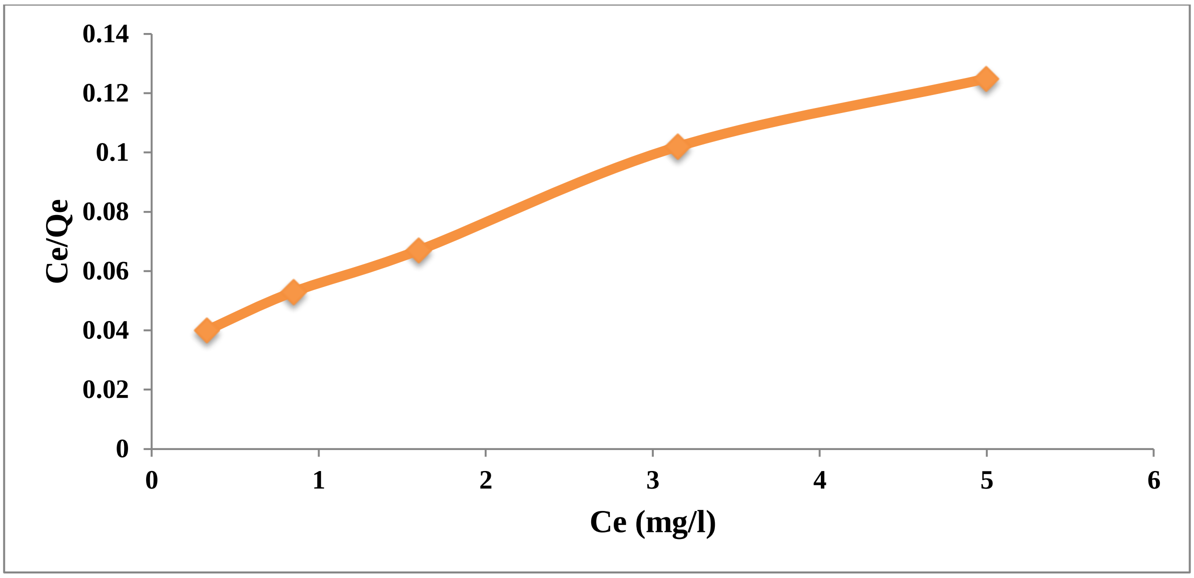

Figure 10(c): Langmuir adsorption isotherm for malachite green for bael shell biosorbent.

4.3.2 Freundlich Isotherm

A graph of log (qe) vs. log (Ce) was drawn for papaya wood to determine Freundlich constants K_f and n_f which shown in the figure 11(a).

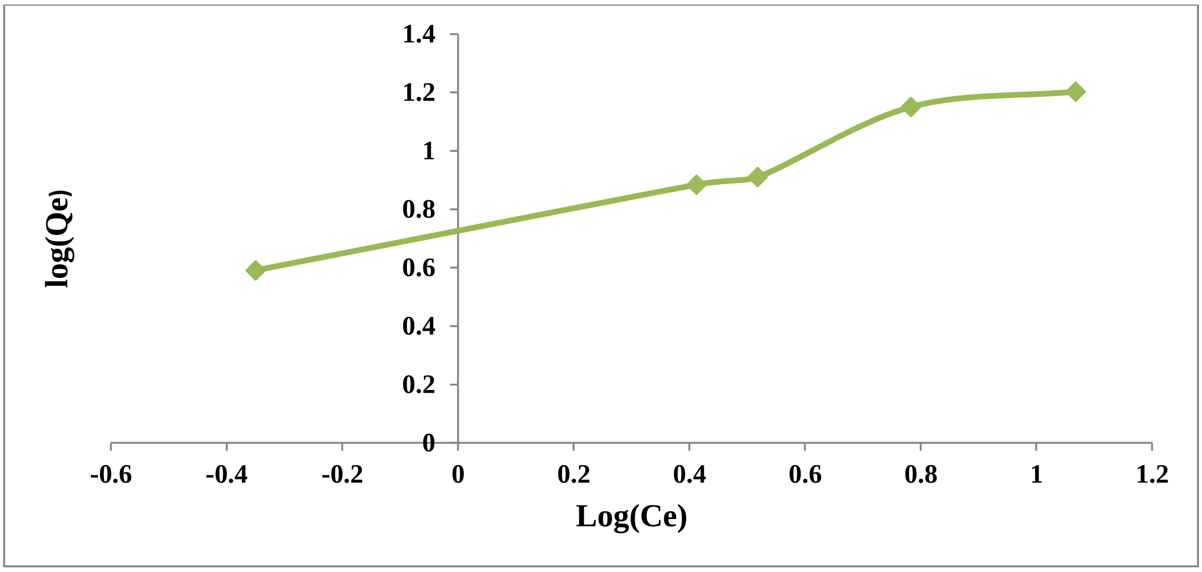

Figure 11(a): Freundlich adsorption isotherm for malachite green dye for papaya wood biosorbent.

A graph of log (qe) vs. log (Ce) was drawn for banana peel to determine Freundlich constants K_f and n_f which is shown in the figure 11(b).

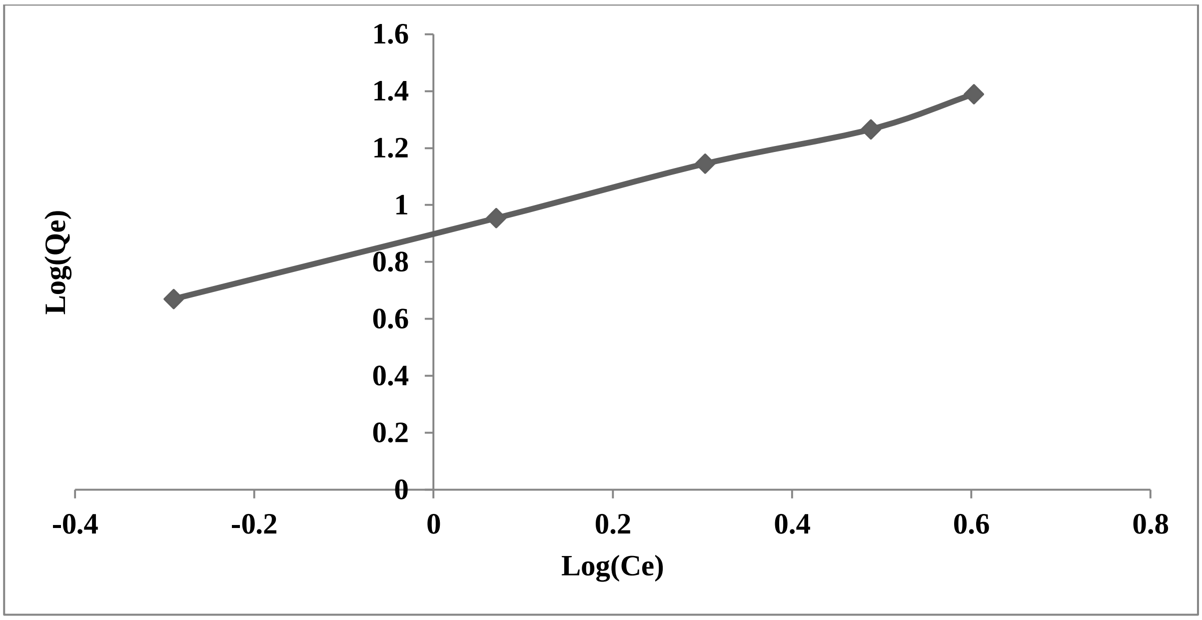

Figure 11(b): Freundlich adsorption isotherm for malachite green dye for banana peel biosorbent.

A graph of log (qe) vs. log (Ce) was drawn for bael shell to determine Freundlich constants K_f and n_f which is shown in the figure 11(c).

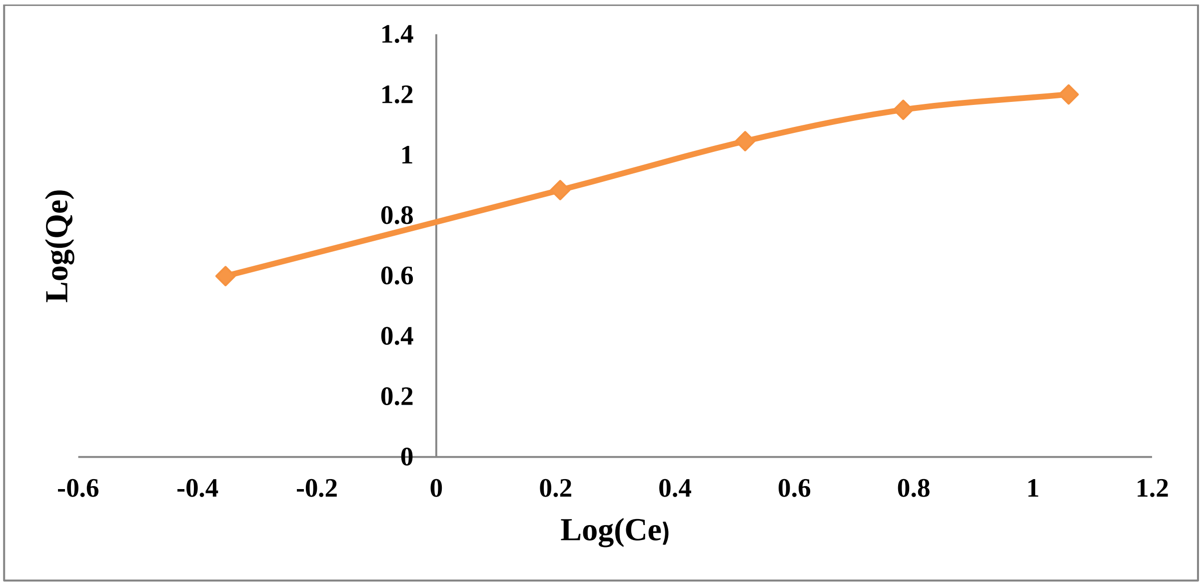

Figure 11(c): Freundlich adsorption isotherm for malachite green dye for bael shell biosorbent.

Table 3: Evaluated adsorption constants at different Isotherm models:

Absorbent	**Langmuir isotherm**			**Freundlich isotherm**		
	R^2	K_L	Qm	R^2	K_F	n_F
Papaya wood	.984	.486	55.55	.998	8.78	.096
Banana peel	.981	4.801	47.61	.998	7.92	1.26
Bael shell	.995	2.48	25.64	.979	6.02	2.27

Qm is Langmuir constant which represents capacity for biosorption and K_L is Langmuir constants which are associated with biosorption energy. Here the value of Qm, KL and R^2 value were obtained by plotting the graph between Ce/Qe and Ce which is mentioned in the figure 10(a), figure 10(b) and figure 10(c) for papaya wood, banana peel and bael shell respectively. These constant values have been mentioned in the table 3. The value Qm showing a better fit of the monolayer Langmuir isotherm to biosorb of malachite green by all three biosorbents. The lower values of K_L are representing the high affinity of dye towards the papaya wood, banana peel and bael shell.

K_F is Freundlich constant which represents capacity for biosorption and nf is Freundlich constants which are associated with intensity of biosorption. Here the value of K_F, n_F and R^2 value were obtained by plotting the graph between Log (Qe) and Log (Ce) which is shown in the figure 11(a), figure 11(b) and figure 11(c) for papaya wood, banana peel and bael shell respectively. The value of K_F, n_F and R^2 have heen mentioned in table 3. The value of Kf and nf are showing the favourable biosorption of malachite green by papaya wood, banana peel and bael shell.

The values of R^2 are indicated as $0 < R^2 < 1$ for favorable, $R^2 > 1$ for unfavorable, $R^2 = 1$ for linear, and $R^2 = 0$ for irreversible to biosorption, respectively. The value of R^2 for different dye concentration used are between 0 and 1 which is showing the ability of malachite green dye biosorption onto papaya wood, banana peel and bael shell.

Chapter 5

Conclusion

FTIR spectra line describes a little modification in the characteristics of surface biosorbent after biosorption as well as before adsorption. Scanning Electron micrographs elucidated that papaya wood, banana peel and bael shell had a remarkable number of pores where there was a fare enough amounts of malachite green dye pigment to be entrapped and biosorbed within these pores. The removal capacity of adsorbent is optimum at pH 10 for papaya wood, at pH 7 for banana peel and at pH 8 for bael shell and declined at higher pH. As the biosorbent dose boosts, biosorption increases due to the availability of free sites. 0.06 g/100 ml concentration of papaya wood, 0.1 g/100 ml of banana peel and 0.12 g/ ml of bael shell are used as the extreme biosorbent dose. As we add biosorbent dose beyond the optimum, the action of biosorption is very less and its cost becomes ineffectiveness. There is a decrease in removal efficiency with increase in initial concentration of dye. The adsorption is directly proportional with the initial concentrations of dye. Maximum removal of dye was achieved at temperature 50°C. Even though the experimental equilibrium outcome is fare enough not only to Langmuir but also to isotherm of Freundlich equations, the Langmuir model considered as the best. The adsorbent was taken in this consideration seems to be very prominent for treatment action on wastewater treatment like in textile, industries dealing with dyes and dyeing and this study confirmed that some biomaterials which are discarded as waste can be used as an efficient biosorbent for dye removal technology.

Scope for future work

Similar work can be carried out for the removal of acid red, methylene blue, acid blue, dyes which are mostly used in textile industry. To know the economy of the process, regeneration studies can be carried out in order. The primary reason for successfull treatment of dye with biosorbent is rapid degradation of relatively much lower toxicity. Further study is required to apply biosorption technique to another stream of waste water bearing different environmental toxic like heavy metals, polyaromatic hydrocarbons, pharmaceutical compounds, etc. In the present investigation attempts were made to synthesise and characterise low-cost biosorbent from brewery industry waste. Since the present investigation has successfully paved ways for the development and application of low-cost biosorbent from industrial waste.

Chapter 6

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